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SUBSTITUTED PHOSPHIRANS

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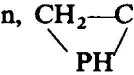
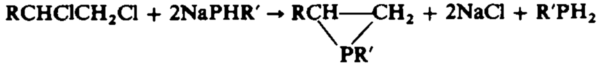
Abstract—Phosphirans bearing substituents at either carbon or phosphorus have been prepared. Their spectral properties are described. The use of hexamethylphosphoramide as a solvent for the preparation of phosphines has been investigated.

Two methods for preparing the novel heterocycle phosphiran,  $\underset{\text{PH}}{\mathrm{CH_2{-}CH_2}}$, were described recently.[1] It has now been established that one of these methods, the reaction of a vicinal dihalide with an alkali-metal phosphinide, is a general reaction for the preparation of C- or P-substituted phosphirans:



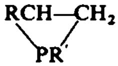
$$\mathrm{RCHClCH_2Cl + 2NaPHR' \rightarrow \underset{PR'}{RCH{-}CH_2} + 2NaCl + R'PH_2}$$

For example, the reaction of 1,2-dichlorobutane with sodium phosphinide in liquid ammonia yields, among other products, a 1:1 mixture of the *cis*- and *trans*-isomers of 2-ethylphosphiran. The constitution of this isomer mixture is established by its ^{31}P NMR spectrum which shows two doublets at high field and with relatively small P—H coupling constants (Table 1). The ^{1}H NMR spectrum (Table 1) and IR spectrum (Table 2) are in accord with the assigned constitution. By analogous reactions *cis*- and *trans*-2-methylphosphiran, 1-methylphosphiran, and 1-phenylphosphiran have also been prepared.

For detailed structural studies, samples of isotopically substituted phosphirans, including phosphiran-P-d were required. Liquid ammonia is clearly not a desirable solvent for this synthesis, since there is a substantial prospect of isotopic exchange with the basic solvent, thus reducing the isotopic purity of the product. So the use of hexamethylphosphoramide (HMPA) as a solvent for the preparation of phosphines and phosphirans was examined. This solvent was recently used for the preparation of some silane and germane derivatives.[2]

Reaction of phosphine with a solution of sodium in HMPA was rapid and led, presumably, to a solution of sodium phosphinide in HMPA. This solution reacted with methyl iodide or ethyl bromide to give good yields of the corresponding primary phosphines. Reaction with allyl bromide gave the new compound, allyl phosphine. Analogously reaction of PD_3 with a solution of sodium in HMPA, followed by addition of 1,2-dichloroethane, gave phosphiran-P-d containing less than 5% of the P—H compound.[3] HMPA has also been used as a solvent in the preparation of phosphiran-2-d, and ^{13}C-enriched phosphiran from suitable isotopically substituted 1,2-dichloroethanes.[3] The isotopically substituted phosphirans have been used in a detailed microwave spectroscopic study of phosphiran.[3]

TABLE 1. NMR SPECTRA OF PHOSPHIRANS,

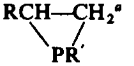


R	R'	$\delta^{31}P$[a]	J_{P-H} (Hz)	δ^1H[b] (Rel. intens.)
H	C_6H_5	234	—	0·3–1·0 (4); 6·5–7·2 (5)
H	CH_3	251	—	0·3–1·8
CH_3	H	—	—	0·1–2·5 (13); –1·4– –2·4 (1)
C_2H_5 (*cis–trans* mixture)	H	271, 288	158, 159	0·2–2·6 (17); –1·3– –2·2 (1)
H	D	—	—	0·3–1·4

[a] ppm upfield from 85% H_3PO_4 (ext).

[b] ppm downfield from internal TMS. All peaks are complex multiplets.

TABLE 2. IR SPECTRA OF



[a]

R = H R' = D	R = H R' = CH_3		R = CH_3 R' = H		R = H R' = C_6H_5[b]
590 (sh)	590 m	1428 s	605 m	1200 s	693 vs (br)
603 m	642 s	1440 m	608 m	1232 m	700 (sh)
616 s	652 (sh)	1445 m	685 vs	1238 m	720 vs (br)
634 s	683 (sh)	2275 m	752 s	1242 m	738 (sh)
650 s	695 s	2285 sh	872 m (br)	1388 m	820 m (br)
911 m	703 s	2835 m	905 (sh)	1395 m	878 m (br)
978 m	788 m	2905 m	912 m	1455 m	912 m
992 s	915 (sh)	2915 s	922 sh	1468 s	1028 m
1007 s	922 s	2925 m	958 m	2285 vs	1045 (sh)
1048 m	934 s	2970 vs	978 m	2290 vs	1055 m
1059 s	942 s	2985 vs	985 m	2295 vs	1070 m
1657 (sh)	950 vs	3010 s	988 m	2760 m	1108 m
1668 (sh)	970 s	3070 m	1000 s	2800 (sh)	1118 m
1675 vs	980 s	3075 s	1015 s	2885 s	1190 m (br)
1680 vs	989 s	3085 m	1023 s	2905 s	1235 m
1692 (sh)	998 s		1065 (sh)	2925 s	1435 s
2795 (sh)	1008 m		1070 m	2950 (sh)	1455 m
2810 m	1032 s		1072 m	2960 (sh)	1485 m
3005 (sh)	1042 s		1140 m	2970 vs	2280 s
3015 s	1050 (sh)		1152 (sh)	2985 vs	2920 m
3030 s	1300 m (br)		1190 (sh)	2995 vs	2950 m
3095 m	1410 s		1195 s	3005 (sh)	3040 m

[a] In cm^{-1}, determined in the gas phase. vs = very strong, s = strong, m = medium, (sh) = shoulder, (br) = broad.

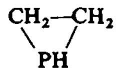
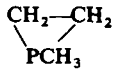
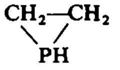
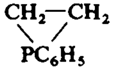
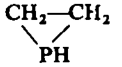
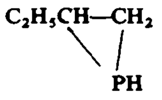
[b] Neat liquid film.

The IR spectra of the new compounds prepared in this work are listed in Table 2. Comparison of the spectra of phosphiran[1] and phosphiran-d allows tentative assignment of the P—H and P—D stretching and deformation modes in these compounds. In phosphiran the P—H stretching mode is at 2279 cm^{-1}, and the P—H deformation mode at 771 cm^{-1}; in phosphiran-P-d the P—D stretching mode is at 1675 cm^{-1}, and the P—D deformation mode is at 616 cm^{-1}. There have been very few assignments of P—H and P—D deformation modes,[4] and a full vibrational assignment of these compounds is currently being undertaken.

The ^1H NMR spectra of the phosphirans are very complex, and have not yet been fully analyzed. Some spectral parameters are reported in Table 1. Those phosphirans which contain a P—H bond show a multiplet signal upfield from TMS, which can be assigned, by considering the integration data, to the upfield portion of a P—H doublet. The low-field part of the doublet falls in the spectral region assigned to the ring C—H protons. It is clear from the spectra of the P-substituted phosphirans, which are of the AA'BB'X type, that inversion at phosphorus is slow on the NMR time scale. This is, of course, in accord with the now well-established configurational stability of tertiary phosphines[5] and other 3-coordinate phosphorus compounds,[6] but the phosphirans are apparently the first examples of secondary phosphines for which this has been shown. Recent work has also demonstrated the configurational stability of a primary phosphine.[7]

The ^{31}P NMR spectra of the C-substituted phosphirans (Table 1) provide additional evidence of configurational stability, since they demonstrate the existence of non-interconverting *cis*- and *trans*- forms of 2-ethylphosphiran. These forms have different ^{31}P chemical shifts and slightly different J_{PH} values, but at the present time it is not possible to decide which of the values should be assigned to the *cis*- and which to the *trans*- isomer.

TABLE 3. EFFECTS OF SUBSTITUTION ON ^{31}P CHEMICAL SHIFTS IN PHOSPHINES[a]

Acyclic phosphines			Phosphirans		
Compound	δ	Δδ	Compound	δ	Δδ
$(CH_3)_2PH$	99·5			341	
		38·5			90
$(CH_3)_3P$	61			251	
$(CH_3)_2PH$	99·5			341	
		53·5			107
$(CH_3)_2PC_6H_5$	46			234	
$(CH_3)_2PH$	99·5			341	
		12·5			53
					70
$(C_3H_7)(CH_3)PH$	87·0			288 271	

[a] Chemical shift values in ppm upfield from 85% H_3PO_4. Data from present work and Refs 1 and 9.

TABLE 4. MASS SPECTRAL CRACKING PATTERNS OF

$$RCH—CH_2 \backslash / PR'$$

R = R′ = H			R = H R′ = D			R = H R′ = CH$_3$			R = CH$_3$ R′ = H					
m/e	Rel. abund.	Prob. comp.	*m/e*	Rel. abund.	Prob. comp.	*m/e*	Rel. abund.	Prob. comp.	*m/e*	Rel. abund.	Prob. comp.	*m/e*	Rel. abund.	Prob. comp.
26	1·2		26	1·0		28	16·3	$C_2H_4^+$	26	5·8		57	35·5	$C_2H_2P^+$
27	6·8		27	6·1		29	5·7		27	32·8	$C_2H_3^+$	58	14·2	$C_2H_3P^+$
28	27·2	$C_2H_4^+$	28	21·2	$C_2H_4^+$	30	9·7		28	3·3		59	6·4	
29	6·8		29	10·1	$C_2H_5^+(C_2H_3D^+)$	32	2·8		29	12·1	$C_2H_5^+$	60	1·2	
30	1·3		30	1·0		33	1·1		31	4·1		61	1·8	
32	6·0		32	5·8		40	2·8		32	4·1		62	13·6	$C_2H_5PH_2^+$
33	6·4		33	2·2		42	36·1	$C_3H_6^+$	33	1·0		63	20·1	$C_2H_5PH_3^+$
34	2·1		34	6·4		44	1·9		34	1·2		64	4·5	
35	7·3		35	3·7		45	11·2	CH_2P^+	35	1·6		65	3·9	
44	1·1		36	5·7		46	39·3	CH_3P^+	36	1·6		68	2·7	
45	8·1		45	7·0		47	60·7	CH_3PH^+	37	3·9		69	3·5	
46	29·9	CH_3P^+	46	23·0	CH_3P^+	48	3·3		38	5·5		71	7·0	
50	2·4		47	11·5	CH_2DP^+	49	20·1	$CH_3PH_3^+$	39	42·9	$C_3H_3^+$	72	11·5	$C_3H_4PH^+$
55	3·4		55	3·3		56	1·1		40	4·7		73	2·7	
56	10·7	C_2PH^+	56	9·2		57	4·9		41	84·5	$C_3H_5^+$	74	100·0	$C_3H_6PH^+$
57	50·8	C_2HPH^+	57	29·6	C_2PD^+	58	36·1	$C_2H_3P^+$	42	5·1		75	3·9	
58	61·0	$C_2H_2PH^+$	58	40·4	C_2HPD^+	59	17·8	$C_2H_4P^+$	43	4·3		76	7·0	
59	3·6		59	38·9	$C_2H_2PD^+$	60	9·7		44	7·4		77	2·1	
60	100·0	$C_2H_4PH^+$	60	5·4		62	1·4		45	30·5	CH_2P^+	78	1·6	
61	2·1		61	100·0	$C_2H_4PD^+$	71	3·8		46	32·9	CH_3P^+			
62	3·1		62	3·8		72	9·1		47	3·1				
						73	2·5		48	13·8	$CH_3PH_2^+$			
						74	100·0	$C_2H_4PCH_3^+$	49	2·9				
						75	3·3		56	3·7				
						76	2·4							

In a recent treatment of ^{31}P chemical shifts[8] the adjustable parameters are taken to be the electronegativities of the substituents on phosphorus, their π-bonding abilities, and the bond angles at phosphorus. The last of these factors can be the only one of significance in the comparison of the chemical shifts of phosphiran and the 2-ethylphosphirans. The $<$ HPC in phosphiran[3] is 98·6°. If it is assumed that in *cis*-2-ethylphosphiran, because of steric interactions between the Et group and the P—H group, the $<$ HPC is larger than that in the *trans*-2-ethylphosphiran, which in turn is larger than that in the parent phosphiran molecule, this would lead to the assignment of the +288 ppm signal to the *trans*-2-ethylphosphiran, and of the +271 ppm signal to the *cis*-compound.

The ^{31}P chemical shift data observed for these phosphirans present a challenge for theories of phosphorus chemical shifts. Although the chemical shifts are all at rather high field compared to other secondary and tertiary phosphines,[9] they span a considerable range for what are apparently minor structural changes. Table 3 indicates that structural changes in phosphirans consistently lead to much larger chemical shift differences than do comparable changes in acyclic phosphorus compounds.

The mass-spectral fragmentation patterns of a number of phosphirans are given in Table 4 (together with some suggested structures for the major peaks observed). The compounds all give molecular ion peaks which are the most intense in the spectrum. Comparison of the spectra of phosphiran and phosphiran-P-d indicates that the ions of *m/e* 58, 57 and 56 from phosphiran probably still contain the PH bond intact, and presumably arise from progressive loss of hydrogen bonded to carbon. When the P—H is replaced by P—CH_3, this course of fragmentation is no longer favored.

Extensive rearrangement is apparent in the spectra of the methyl phosphirans. A major peak at *m/e* 42 in the spectrum of 1-methylphosphiran must be assigned to the ion $C_3H_6^+$, and ions formulated as $C_2H_5PH_2^+$ and $C_2H_5PH_3^+$ appear in the spectrum of 2-methylphosphiran.

EXPERIMENTAL

PMR spectra were determined on a Varian A-60 spectrometer. ^{31}P NMR spectra were determined on a modified Varian V-4300 spectrometer at 24·3 MHz. IR spectra were determined on Beckman Model IR12 and IR5 spectrophotometers. Mass spectra were determined on a CEC model 21–620 mass spectrometer, accelerating voltage 70 V.

Because of their marked thermal instabilities, the phosphirans prepared were characterized by their spectral properties, and not by elementary analyses. All manipulations of phosphirans were carried out on a conventional vacuum line in the absence of oxygen and moisture.

Hexamethylphosphoramide (HMPA) was distilled from Na at reduced press. All other reagents and solvents were research grade commercial materials purified by distillation.

Preparation of phosphirans in liquid ammonia

1-*Methylphosphiran.* Freshly cut Na metal (1·4 g, 0·061 mole) was placed in a stainless steel bomb (150 ml) under an atm of dry N_2. The bomb was then connected to a vacuum line and evacuated. Liquid ammonia (25 ml) and methylphosphine (0·064 mole) were condensed into the bomb which was then allowed to warm up. After standing at room temp for 1 hr with occasional shaking, the bomb was cooled in liquid N_2, and the H_2 gas produced in the reaction was removed by pumping through the vacuum line.

1,2-Dichloroethane (3·4 g, 0·034 mole) was condensed into the bomb which was once more allowed to warm. As soon as it reached between −10° and 0°, the bomb was shaken and the reaction mixture quickly transferred to the vacuum line and fractionated through traps at −63°, −95°, and −196° to remove liquid ammonia and methylphosphine. The remaining mixture was then slowly fractionated through traps at −45°, −63°, −82° and −196°. The −82° fraction consisted of the desired product 1-methylphosphiran and a small amount of 1,2-dichloroethane. This fraction was recycled through the traps and the process was repeated until a pure sample of 1-methylphosphiran was obtained, yield: 30%.

Alternatively, the desired product could be isolated by gas chromotography,[1] but with much poorer yields.

2-*Methylphosphiran*. The preparation of this compound was carried out in a stainless steel bomb as for 1-methylphosphiran.

In this case, sodium metal (1·55 g, 0·0674 mole), phosphine (0·070 mole), liquid ammonia (25 ml), and 1,2-dichloropropane (4·2 g, 0·037 mole), were used. The reaction mixture was fractionated on the vacuum line through traps at −22°, −63°, −78°, −95° and −196°. The −63° fraction consisted of the desired product 2-methylphosphiran and a very small amount of 1,2-dichloropropane, and this fraction was recycled through the traps and the process repeated until a pure sample of 2-methylphosphiran was obtained, yield 30%.

2-*Ethylphosphiran* was prepared in an analogous way in 25% yield from 1,2-dichlorobutane, and condensed in a trap at −63°.

1-*Phenylphosphiran*. Freshly cut Na metal (2·3 g, 0·10 mole) was placed in a 2-neck flask (250 ml), in an atmosphere of dry N_2, which was fitted with a dropping funnel containing phenylphosphine (0·10 mole) and a magnetic stirrer. The flask was evacuated on the vacuum line and liquid ammonia (about 75 ml) was condensed into it to dissolve the Na. The deep blue Na soln was kept at a temp below the b. p. of ammonia with a dry-ice–$CHCl_3$ bath. Phenylphosphine was added dropwise to the soln which gradually turned yellow at the end of the addition, while H_2 gas produced in the reaction was slowly removed by pumping.

1,2-Dichloroethane (5 g, 0·05 mole) was then added dropwise through the dropping funnel into the yellow soln which immediately became thick and milky. Removal of liquid ammonia on the vacuum line left behind a white residue.

Diethyl ether was then added to extract the product from the residue. The mixture was filtered using a Skau tube, and the ether was evaporated from the filtrate on the vacuum line to leave behind a liquid residue. 1-Phenylphosphiran was isolated from this liquid residue by distillation under reduced pressure, b.p. 44–48/1·5 mm; yield 60%.

Preparation of phosphines in HMPA

Finely dispersed Na (5 μ) in xylene (1·1 g Na, 0·048 moles) was placed in a 1 l. bulb and the xylene was pumped out and replaced by HMPA (75 ml). Phosphine, at a pressure of 60 cm, was admitted to the bulb, and the mixture was shaken. PH_3 and H_2 were pumped out, and PH_3 readmitted. This procedure was repeated until the initially blue mixture became clear yellow, with no trace of residual Na. The soln was then cooled in liquid N_2 and the alkyl halide (0·048 mole) condensed into it. The mixture was slowly warmed to room temp and the volatile products were fractionated in the vacuum line.

MeBr yielded methylphosphine (68%), condensing in a trap at −130°. EtCl yielded ethylphosphine (78%) condensing in a trap at −130°. These phosphines were characterized by IR and NMR spectra.

Allyl bromide yielded allylphosphine (55%) which was separated from other products by gas chromatography on the system previously described[1] (retention volume 420 ml He at 35°). This new compound is characterized by its ^1H NMR spectrum: $\underline{H}_2C{=}$, $\delta = 4{\cdot}95$, mult; $={C}\underline{H}$, $\delta = 5{\cdot}5$–$6{\cdot}35$, mult; $C\underline{H}_2P$, $\delta = 2{\cdot}0$–$2{\cdot}5$, mult; $P\underline{H}_2$, $\delta = 2{\cdot}74$, mult, $J_{PH} = 193$ Hz; and by its IR spectrum: ν_{P-H}, 2300 cm^{-1}; $\nu_{C=C}$, 1640 cm^{-1}.

The use of HMPA in the preparation of phosphirans is described in Ref.[3]

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